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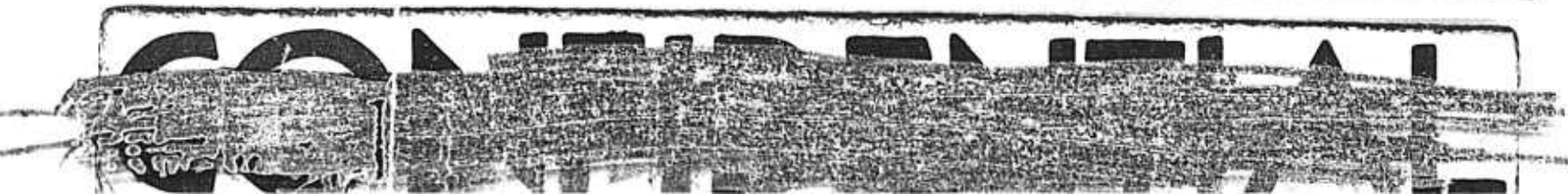

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FINAL REPORT

Contract Number DA-33-019-ORD-766

on

A RESEARCH INVESTIGATION OF POSSIBILITIES FOR OBTAINING HOT-HARD ELECTRODEPOSITED [illegible]MIUM OR CHROMIUM-BASE ALLOYS FOR CANNON

FC

to

WATERTOWN ARSENAL

W.A.L. File No. 691.1/25/84

August 9, 1955

by

William H. Safranek, Donald E. Swickard,
Harry L. Moore, and Charles L. Faust

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FINAL REPORT

Contractor: Battelle Memorial Institute

Contract Number: DA-33-019-ORD-766

Title of Project: "A Research Investigation of Possibilities for Obtaining Hot-Hard Electrodeposited Chromium or Chromium-Base Alloys for Cannon"

W.A.L. File Number: 691.1/25-84

Date: August 9, 1955

Technical Supervision: This project is being performed under the technical supervision of Watertown Arsenal Laboratory

Ordnance District: Cleveland, Ohio

O. O. Project Number: TR3-3003B

D/A Project Number: 501-01-004

Object: To investigate hot-hard chromium-iron-alloy electroplate for lining gun tubes

Authors: William H. Safranek, Harry L. Moore, Donald E. Swickard, and Charles L. Faust

Summary: A process was developed for reproducing continuous, crack-free chromium-iron-alloy plate on the bore surface of erosion-gage weapon inserts. Firing tests revealed satisfactory adherence of the plate on some inserts. The plate on other inserts was adherent, except for small patches of nonadherent plate on each, which likely can be prevented during future work by increasing the pH of the bath. Other inserts were plated with conventional chromium for comparing the erosion resistance of the chromium-iron alloy with that of chromium. Hot-hardness data forecast a better erosion resistance for the chromium-iron alloy.

Several improvements were developed in the plating process during the course of this research. A recent development incorporated in the procedure for plating inserts constituted an activating treatment for the steel to inhibit passivation during the first few seconds of plating. Firing-test data on inserts so treated are incomplete. However, laboratory data on the adherence of the plate showed a marked improvement in the reproduction of good adherence. A simplified process for obtaining improved adherence without heat treatment was successful for plating a cannon-steel flat panel

but has not yet been evaluated for plating erosion-gage weapon inserts. Another recent development was the improvement in the reproducibility of continuous adherent plate on rifled inserts brought about by increasing the pH of the plating bath to compensate for the turbulence in agitation caused by the rifling.

Conclusions: Until firing tests are completed for comparing the erosion resistance of the chromium-iron alloy with that of conventional chromium plate, any conclusion on the merit of plating weapons with chromium-iron alloy would be premature. However, the research should be continued in view of the encouraging adherence and hot-hardness data available at the present time. The best conditions developed to date should be investigated for plating 40-mm sections, which can be evaluated with better precision than the erosion-gage weapon inserts.

Report Period: This report covers the period from February 10, 1952, to August 9, 1955. The laboratory work was recessed about July 15, 1955, pending the completion of contractual arrangements for continuing the research.

Fiscal Data: On August 9, 1955, approximately 100 per cent of the contract was completed.

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A RESEARCH INVESTIGATION OF POSSIBILITIES FOR OBTAINING HOT-HARD ELECTRODEPOSITED CHROMIUM OR CHROMIUM-BASE ALLOYS FOR CANNON

by

William H. Safranek, Donald E. Swickard,
Harry L. Moore, and Charles L. Faust

SCOPE OF WORK

This project is a continuation of a research program for the development of hot-hard chromium-iron-alloy electrodeposits in an attempt to achieve a crackfree erosion-resistant plating for gun tubes.

Several objectives as defined in the original contract were as follows:

(a) Design and development of equipment for applying chromium-alloy electroplates to gun-bore surfaces toward effective application of alloy plate in full-length gun tubes.

(b) Establishment of technical instructions and specifications for the application to cannon of any significant new developments which have been completed to a suitable stage.

(c) Evaluation of new processes, as requested by technical representatives of the Ordnance Corps and mutually agreed upon.

Objectives added by the first contract amendment dated May 29, 1952, were as follows:

(d) Development of adhesion of improved alloying for hot hardness.

(e) Study of methods of alloy-bath replenishment and of improving the plating efficiency.

(f) Development of a specification for chromium salt to be used in the alloy plating bath.

The third amendment dated April 7, 1953, included the following objectives:

(g) Supplying technical services in connection with the plating of the chromium-iron alloy at Watervliet Arsenal. This may

include selection of anode materials, specifications, and sources of plating chemicals, as well as furnishing of technical instructions on control of electroplating conditions and control of impurities.

(h) Conduct of further research on adherence of the chromium-iron alloy to cannon steel, including study of the influence of heat treatment on properties of the deposits.

(i) Comparison of the 94 per cent chromium-6 per cent iron alloy deposit with the 85 per cent chromium-15 per cent iron alloy deposit.

(j) Conduct of research on electroforming chromium-iron cannon inserts, with and without iron-plate backup, including consideration of the mechanical characteristics of the electroformed materials, by control of alloy composition, heat treatment, etc.

The fourth amendment dated April 2, 1954, included the following:

(k) Conduct further research on the properties of alloy electroplate as related to the composition of the alloy in the range of 85 per cent or more chromium and balance iron, including stress measurements.

(l) Conduct further research on the procedure for plating chromium alloy on gun tubes, including a study of new or improved methods for preparing cannon steel surfaces for receiving adherent plate, and a study of the distribution of chromium-alloy-plate thickness on gun-tube-bore surfaces.

(m) Conduct further research on electroforming chromium-iron-alloy cannon inserts, including consideration of alloy composition for control of properties.

Objectives (a), (d), (e), (f), (g), (h), (i), (j), (k), (l), and (m) received the major emphasis during the course of the research. The effort on objectives (a), (g), and (l) related chiefly to plating erosion-gage weapon inserts. The limited effort on plating 40-mm sections was not definitive. Relative to Objective (b), technical instructions and recommendations for plating inserts were forwarded to Watertown Arsenal and are summarized again in this report.

INTRODUCTION

Previous research on chromium-iron-alloy electroplating* resulted in a procedure for depositing an alloy that did not soften appreciably after heating to 1200 F. Hot hardness appeared to be within reach. The plating bath comprised principally a trivalent chromium salt, instead of the chromic acid contained in the conventional chromium bath. The plating efficiency was 5 to 10 times greater in the trivalent solution, and the alloy could be deposited at a higher rate.

The alloy plate was without the crack system of conventional chromium. However, the plate on erosion-gage weapons became cracked during firing tests. The firing tests caused the plate to spall off the bore surfaces, indicating inferior adherence. Research work was aimed, therefore, at improving the properties of the plate and its adherence to cannon bore surfaces.

Early work indicated that adherence could be improved by electropolishing the bore surfaces prior to plating, combined with heat treating after plating. The plating-bath formulation w s modified, giving better filling of the plate into the machining scratches in the bore surfaces of the available test weapons. The modified bath formulation also resulted in a reduction in the stress in the plate. The principal modification was the change in the chromium salt from a basic chromium sulfate containing sodium to chromium ammonium sulfate.

After the bath formulation was changed, a number of test weapons were plated in accordance with a recommendation from Watertown Arsenal. Changes in the current density were investigated. Alloy plate containing about 94 per cent chromium and 6 per cent iron was compared with alloy plate containing about 85 per cent chromium and 15 per cent iron.

*Final Technical Report on "A Research Investigation of Possibilities for Obtaining Hot-Hard Electrodeposited Chromium or Chromium-Base Alloys For Cannon", Battelle Memorial Institute, February 9, 1952 (Contract No. DA-33-019-ORD-9);
Interim Technical Reports on "A Research Investigation of Possibilities for Obtaining Hot-Hard Electrodeposited Chromium or Chromium-Base Alloys For Cannon", Battelle Memorial Institute, September 1, 1950, September 15, 1951, and January 15, 1952 (Contract No. DA-33-019-ORD-9);
Final Technical Report on "A Research Investigation of Possibilities for Obtaining Hot-Hard Electrodeposited Chromium or Chromium-Base Alloys for Cannon", Battelle Memorial Institute, November 15, 1949 (Contract No. W33-019-ORD-6397).

EXPERIMENTAL DATA*

Plating Erosion-Gage Weapon Inserts With Chromium-Iron Alloy

Development of Improved Procedures

During the course of the research under the subject contract, erosion-gage weapon inserts were plated with chromium-iron alloy many times, using the best knowledge available each time for improving the properties and the adherence of the alloy plate. Several improvements were made during this contract period. Some of them were initiated, first, by plating flat panels of cannon-stock steel, and incorporated, later, in the process for plating inserts. Other improvements related to fixture design for the inserts. The important improvements were as follows:

(1) The modification of the plating bath and the plating conditions to exclude ferric iron in the solution improved the adherence of the plate and reduced the incidence of cracking in the chromium-iron alloy during heat treatment after plating. A platinum-clad, silver anode was adopted, instead of a lead-plated copper anode, to avoid the oxidation of ferrous to ferric iron at the anode surface. The temperature of the plating bath was lowered to 115 F, and the cathode current density was changed to about 100 amp/sq ft, to increase the rate of cathodic reduction of ferric to ferrous iron. Thus, ferric iron build-up in the plating bath was eliminated by balancing the anode and cathode conditions. These developments were described in detail in the Interim Reports dated October 1, 1952, and April 9, 1953.

(2) The development of an anode fixture providing for a uniform solution flow through the bore of the insert improved the continuity of the alloy plate. The gasses evolved at the anode and cathode caused defective plate, unless they were removed by pumping solution through the bore at a regular rate. Either this solution must be filtered to avoid nodular deposits, or the plating bath must be filtered with an auxiliary pumping system. Turbulent agitation at bore surfaces must be avoided so as to eliminate flaky deposits. The fixture developed for plating inserts included a reducing chamber for eliminating turbulence. This fixture was detailed in Appendix B in the Interim Report dated October 9, 1954.

*The data were recorded in the following laboratory record books:

No. 6695, pages 1 to 100
No. 7121, pages 14 to 23
No. 7917, pages 1 to 41
No. 7989, pages 1 to 100
No. 8799, pages 1 to 100
No. 9509, pages 1 to 100
No. 10,160, pages 1 to 74.

(3) A test was established for distinguishing satisfactory from inferior adherence. The chisel test used previously was unsatisfactory for revealing a poor bond that would be disclosed by one or two rounds of test firing. The impact and saw-break tests described in Table 3, page 15, in the Interim Report dated April 9, 1954, was adopted after the chisel test was discredited. Segments about 1/4 inch thick were sawed off the muzzle end of each insert after plating and heat treating. Since the inpact and saw-break tests were developed, inserts with good adherence based on the laboratory tests have been satisfactory with respect to adherence in firing tests. Even inserts with a doubtful adherence, according to the impact and saw-break tests, were satisfactory in firing tests. One such insert was No. 180X, fired for 10 rounds. The available information indicates that the impact and saw-break tests constitute a more severe test for adherence than does 10 rounds of firing.

(4) Electropolishing improved the adherence of chromium-iron alloy plate on cannon steel and the thickness uniformity of the plate on lands and grooves in rifled inserts. Smeared, highly stressed metal, introduced at the surface by machining the bore, was removed and surface irregularities were smoothened. By rounding off the edges of the lands, excessive build-up at edges by plating was avoided. The contour of representative lands after electropolishing and plating was shown in Figures 1 and 2, page 5, and Figure 9, page 22, in the Interim Report dated April 9, 1954. The electropolishing procedure is detailed in Appendix A of this Final Report.

(5) Increasing the iron content from about 6 to between 10 and 15 per cent improved the properties of the alloy plate. Plate containing only about 6 per cent iron, balance chromium, on the bore surface of erosion-gage weapon inserts and 40-mm sections, frequently cracked either spontaneously or during heat treatment, after plating. On the other hand, the incidence of such cracking was considerably reduced by increasing the iron and reducing the chromium contents of the alloy, as detailed in the experimental section of the Interim Report dated April 9, 1954.

(6) The improved resistance to cracking is associated with a reduction in the tensile stress in the chromium-iron plate when it is deposited on steel. The increase in the iron content of the plate and the iron concentration in the plating bath reduced the stress, as shown in Figure 4, page 11, in the Interim Report dated October 9, 1954. Other factors influence the stress, as described on pages 34 to 39 in the Interim Report dated April 9, 1954. For example, the plate was stressed less when the chromium concentration of the bath was between 32 and 45 g/l than it was when the chromium concentration was raised to 65 g/l. Adding 30 g/l of boric acid to the bath greatly reduced the stress. However, the cathode current efficiency was reduced to only 14 per cent, so the boric acid addition did not appear to be practical. A smaller addition of 0.5 to 10 g/l did not reduce effectively the stress in the plate.

(7) The recognition of the effects of impurities in the plating solution was important in developing the process for reproducing dense, continuous, chromium-iron alloy deposits. Copper, lead, silicon, and other metallic impurities cause defective plate, and/or a reduction in the cathode efficiency and throwing power, as described in detail on pages 42 to 44 in the Interim Report dated April 9, 1954. The necessity for removing inorganic and organic impurities from newly prepared solutions became apparent soon after undertaking the research under the subject contract. With the activated-carbon treatment described in Appendix A in the Interim Report dated October 9, 1954, followed by electrolytic purification for 1 or 2 hours, continuous and dense deposits can be obtained in new solutions. The activated-carbon treatment was also beneficial in eliminating pitting in plates deposited from aged baths. This pitting probably was caused by an organic contamination.

(8) Adding ammonium sulfamate to the plating bath increased the buffering action of the solution, inhibited the anodic oxidation of ferrous to ferric iron, and improved the adherence of the plate to cannon-steel panels. Therefore, a 60 g/l addition was incorporated in the bath used subsequently for plating inserts. Since this modification was adopted, dense, crackfree chromium-iron plate has been produced more consistently. The results of the initial tests with ammonium sulfamate additions were summarized on pages 2 to 4 in the Interim Report dated October 9, 1954.

(9) Good adherence was reproduced with greater frequency after an activating treatment was adopted immediately before plating. The treatment consisted of a 1-minute dip in a solution containing 18 ml/l of 95 per cent sulfuric acid.* The inserts were transferred without rinsing in water to the plating bath after activation. Before adopting this treatment, a film of hydrated ferrous oxide, identified by X-ray diffraction, was formed on cathode surfaces during the first 15 seconds after plating was started. The thickness of the oxide film was influenced by several factors including the pH of the bath, the current density, and the kind of chromium complex compounds. At best, the film could be diffused by heat treatment at 750 F for 2 or 3 hours, after plating. In some cases, the heat treatment caused the plate to become adherently attached to the steel, judging by saw-break tests. However, the thickness of the film evidently was excessive at other times, because the adherence after heat treatment was unsatisfactory. For example, the plate was adherent on only six among nine panels plated without the activating dip. However, the plate was adherent on eight among nine panels in another group plated after activation. The ninth panel was blistered before heat treatment, but the cause for the blisters is not known.

*Several other treatments were investigated during the course of the research on improving adherence. The results of all treatments are summarized in Appendix B.

Table 1 details the results of testing the adherence of chromium-iron plate on representative erosion-gage weapon inserts plated after activation. Good adherence was indicated on most of these inserts. The dilute sulfuric acid dip was used for activation in some cases, but, for other inserts, activation was accomplished by using a quick water rinse after dipping 1 minute in a 10 per cent solution of hydrochloric acid. Table 1 also details the procedure for plating the inserts.

(10) Good adherence without heat treatment was obtained by treating cannon steel anodically for 5 minutes at 100 amp/sq ft in a 42 per cent solution of phosphoric acid. The phosphoric acid anodizing step was inserted between the second cleaning operation (Step No. 4 in Appendix A) and the dilute sulfuric acid-activating operation (Step No. 5 in Appendix A). Metallographic examination after the saw-break test revealed good adherence for the first time without heat treatment after plating. The phosphoric acid anodizing treatment was so recent a development that no opportunity occurred to use it for plating erosion-gage weapon inserts during the period covered by the subject contract.

(11) Increasing the pH of the plating bath eliminated the flaky deposits obtained previously on the bore surface of the muzzle (top) end of the rifled inserts. With a pH of 2.0, or less, the turbulence in agitation introduced by the rifling caused such defective deposits. However, a pH of 2.1 to 2.4 compensated for the turbulent agitation, resulting in continuous crackfree plate without defects. A few blisters were observed on the bore surface of the breach end (bottom) of an insert plated while the pH was adjusted to 2.6. Table 2 details the results of investigating pH changes for plating rifled erosion-gage weapon inserts. Several defective plates produced before identifying the optimum pH range for rifled inserts were attributed to a deficient pH.*

Results of Firing Tests

Sixteen erosion-gage weapon inserts were submitted to Watertown Arsenal for firing tests. The firing test was extended to 195 rounds on one rifled insert with satisfactory performance. Among 11 others that have been tested to date, 3 were satisfactory with respect to the adherence of the plate. The plate on 4 other inserts was adherent except for small patches on each. These patches might have been caused by a deficient pH, which can be corrected by increasing the pH in accordance with information obtained recently.

Unsatisfactory adherence on one side of the bore was reported for one insert. The plate on two inserts was reported to be nonadherent, but no

*Appendix C summarizes the procedures recommended for plating chromium-iron alloy on erosion-gage weapon inserts.

TABLE 1. DATA ON PLATING EROSION-GAGE

Insert Number[b]	Chromium Concentration, g/l[c]	Iron Concentration, g/l[c]	pH	Plating Time, hr	Plate Thickness, in.	Condition of Chromium-As Deposited
185X(3)	31.0	0.85	1.95	1-3/4	0.0037	Continuous, a few dark streaks
177X(2)	35.0	0.84	1.95	2	0.0031	Continuous, a few fine cracks near muzzle end
176X(3)	40.0	0.85	1.95	2	0.0034	Ditto
209X(3) (Rifled)	31.5	0.85	1.99	2-1/4	0.0030	Continuous, one crack on lands
229X(1)	40.0	0.79	1.95	2-1/4	0.0030	Crackfree, continuous except for top 5/8-inch due to short anode
225X(1)	40.0	0.80	2.0	2-1/4	0.0028	Crackfree, continuous except for bottom 1/4-inch due to lack of spacer
222X(1)	39.0	0.81	2.0	2	0.0025	Continuous and crackfree
220X(1) (Rifled)	38.0	0.80	1.95	3-3/4	0.004(M) 0.005(B)	Continuous except for 1-1/2 inches at muzzle end
217X(4) (Rifled)	41.0	0.85	2.05	4-1/2	0.005(M) 0.0065(B)	Continuous and crackfree
218X(4) (Rifled)	41.0	0.85	2.1	4-1/2	0.005(M) 0.0065(B)	Continuous and crackfree, a few dark streaks

Footnotes appear on the following page.

WEAPON INSERTS WITH CHROMIUM-IRON ALLOY[a]

Alloy Deposit[d] After Heat Treatment	Test Results After Heat Treatment[e]			
	Chisel Test[f]	Saw-Break Test		Knoop Hardness (100-g Load)
		Before Impacting[g]	After Impacting[h]	
No change	Adherent	Adherent	Adherent	556-625
Many fine cracks	"	Adherent, many fine cracks	No change	560-590
Ditto	"	Ditto	Two of six edges uncertain	618-631
Flaky in grooves next to lands, many fine cracks	"	"	Ditto	Not determined
Many fine cracks	"	Adherent	Adherent	505-642
Ditto	"	Adherent, a small section of plate missing	Nonadherent, flaked off at edges	564-642
No change	"	Adherent, five of six edges were adherent	Adherent	530-652
Dark in grooves next to lands	"	Nonadherent in grooves next to lands, three of six edges adherent	Spalled slightly on two edges	518-575
No change	"	Adherent	Adherent	551-625
No change	"	"	"	560-600

Footnotes for Table 1

(a) The procedure for cleaning and electropolishing the inserts prior to plating with chromium-iron alloy is given in Appendix A. The bath was dummied with a 2 x 5-inch panel at 100 amp/sq ft prior to plating each insert. The current density for the inserts was also 100 amp/sq ft. The temperature was 113 to 118 F. Solution was pumped through each insert at the rate of 0.29 gal/min. The circulating pump was lined with Neoprene; the pump used for filtering the bath continuously was of stainless steel; the filter chamber was of Lucite; the filtering medium was a cotton fiber tube (fine grade) made by the Sethco Manufacturing Company. The filter tube was coated with a mixture of activated carbon, and a purified wood-cellulose filter aid. The plating tank was a glass jar, 24 inches high and 12 inches in diameter. No ferric iron was detected at any time.

(b) Many of the inserts were plated previously with chromium-iron alloy, which was stripped in 35 per cent hydrochloric acid solution. The causes of the poor deposits and their frequency were as follows:

Low pH for 11 inserts	Low temperature for 1 insert
Bent anode for 2 inserts	Low current density for 1 insert
Turbulent agitation for 1 insert	Other causes for 3 inserts

After stripping, each insert was heated (in a nitrogen atmosphere) to 350 F for 15 hours to drive out hydrogen. The figure in parentheses denotes the number of times that each insert was plated.

(c) The chromium and iron concentrations were determined before plating each insert, using the procedures given in Appendix C. The procedure for the preparation of the 36-liter bath is also given in Appendix C.

(d) The bore surfaces were examined with a boroscope magnifying about 5 diameters. The heat treatment after plating was 1 hour at 350 F and 3 hours at 750 F in a hydrogen atmosphere.

(e) The heat treatment was in a hydrogen atmosphere for 1 hour at 350 F and then 3 hours at 750 F.

(f) The edge of a 1/16-inch-wide chisel was driven into segments sawed from each insert near the interface between the plate and steel. The chips and chipped areas were examined microscopically to determine where cleavage occurred.

(g) Using a 1/4-inch-thick segment carved off the muzzle end of each insert, a saw cut was made in a plane perpendicular to the bore from the outer surface of the ring toward the plated bore surface. After sawing to within about 1/64 inch from the chromium-iron plate, one-half of the ring was broken away from the other half by a blow with a hammer. The fracture zone was examined metallographically for evidence of poor or good adherence of the plate.

(h) Using a 1/4-inch-thick segment sawed off the muzzle end of each insert, a hardened-steel pin was driven into the bore by the impact of a 12-pound weight falling 21 feet. The pin was pressed into the bore further with an arbor press with a pressure of 10,000 psi.

TABLE 2. EFFECT OF pH CHANGES ON THE PLATING OF RIFLED EROSION-GAGE INSERTS WITH CHROMIUM-IRON ALLOY [a]

Insert Number	Chromium Concentration, g/l	Iron Concentration, g/l	pH	Plating Time, hours	Quick Rinse or Dilute Acid Dip	Condition of Chromium-Iron-Alloy Deposit	
						On Erosion-Gage Insert	On a Control Panel
217X(4)[b]	41	0.85	2.05	4-1/2	Dilute acid dip	Continuous and crackfree, 1 pit about at center of insert in a groove, a few tiny nodules in grooves	Good deposit, gray, no flaky or cracked areas
218X(4)[b]	41	0.85	2.10	4-1/2	Ditto	Continuous and crackfree, a few black streaks running parallel to length	Slighly burned on corners, otherwise a good deposit
209X(4)	39	0.95	2.25	1-1/12	Quick Rinse	Continuous and crackfree, no defects	Corners burned on about a 1-inch radius
209X(5)	39	0.95	2.4	1-1/12	Dilute acid dip	Continuous and crackfree, one small blister in breach; bottom spacer had small unplated area and many black streaks	Corners badly burned, also many light and dark-gray streaks, a few black streaks
209X(6)	40.3	0.97	2.6	1-1/3	Quick Rinse	Continuous and crackfree, a few black streaks and small blisters in the breach; bottom spacer was almost entirely unplated	Corners badly burned, bottom-half of panel covered with light- and dark-gray streaks; no plate on top half

(a) The procedures used to plate these deposits were identical to those described in Table 1.
(b) These inserts are also listed in Table 1, but are given here for comparison purposes.

details are available on the extent of the inferior adherence, or the number of rounds of test firing. The results of the firing tests are compared in Table 3 with the results of the laboratory adherence tests. Figure 1 is a photomicrograph of a section of an insert that appeared to be plated adherently, judging by the saw-break and impact tests, but which showed a small patch of nonadherent plate after firing 37 rounds. Figure 2 illustrates doubtful adherence of the plate on another insert, which also showed a patch of nonadherent plate after firing 60 rounds. Firing tests on 4 inserts had not been started by the time this report was prepared.

One smooth-bore insert and one rifled insert were plated with conventional chromium for comparison in firing tests with the inserts plated with the chromium-iron alloy. The plating conditions for these inserts (Nos. 224X and 216X) are given in Appendix D.

Electroforming Erosion-Gage Weapon Inserts

Plating dense, crackfree chromium-iron alloy on the outside of flat panels and cylindrical tubing has been more consistent throughout this project than plating on the bore surfaces of test weapons. Thus, electroforming the chromium-iron alloy by depositing it on the outer surface of a cylindrical mandrel appeared a promising method of manufacturing erosion-resistant cannon liners.

Smoothbore inserts were fabricated by plating chromium-iron alloy on copper mandrels, backing up the chromium-iron alloy with electrodeposited nickel, and dissolving the copper in nitric or chromic acid solution. Copper was selected for the mandrels to expedite their preparation. In order to produce electroformed liners at a lower cost, a low-melting alloy mandrel could be cast in a steel mold and melted out after the electroforming operation. The low-melting alloy could be used again for casting more mandrels.

The procedures for electroforming three liners were described on pages 26 to 29 in the Interim Report dated April 9, 1954. A soft nickel was electrodeposited over the chromium-iron alloy on two liners. These liners were not test fired, because of the softness of the nickel, which was in the range of 167 to 187 Knoop (100-gram load). Very hard nickel (506 to 581 Knoop with a 100-gram load) was used for the third liner. Several cracks extending through the nickel and chromium-iron alloy layers were detected by treating with a fluorescent penetrant and examining under black light after the outer surface was machined to a diameter of 1.125 inches.

Medium-hard nickel (422 to 387 Knoop with a 100-gram load) was deposited on the fourth liner, which was electroformed by the procedure described in Appendix E. Four short radial cracks were detected in the

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FIGURE 1. PHOTOMICROGRAPH OF CROSS SECTION OF EROSION-GAGE WEAPON INSERT NO. 185X AFTER IMPACT AND SAW-BREAK TESTING, ILLUSTRATING GOOD ADHERENCE OF THE CHROMIUM-IRON ALLOY PLATE

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FIGURE 2. PHOTOMICROGRAPH OF CROSS SECTION OF EROSION-GAGE WEAPON INSERT NO. 176X AFTER IMPACT AND SAW-BREAK TESTING, ILLUSTRATING DOUBTFUL ADHERENCE OF THE CHROMIUM-IRON ALLOY PLATE

TABLE 3. RESULTS OF FIRING TESTS ON EROSION-GAGE WEAPON INSERTS PLATED WITH CHROMIUM-IRON ALLOY

Insert Number	Approximate Composition of Plate	Plating Procedure	Results of Impact and Saw-Break Tests on Segment Sawed Off Muzzle End	Number of Rounds in Firing Test	Results of Firing Tests
69X	Not determined	(a)	Not tested	60	Satisfactory adherence; a few cracks
149X	About 94% Cr-6%Fe	(b)	Ditto	10	Patches removed on lands and grooves in chamber section; muzzle half undamaged
164X	Ditto	(b)	"	10	Good adherence
179X	About 85% Cr-15% Fe	(c)	Doubtful adherence	5	Extensive plate removal at muzzle end
180X	Ditto	(c)	Ditto	10	Satisfactory adherence
181X	About 90% Cr-10% Cr	(c)	Not tested	5	Poor adherence
182X	About 85% Cr-15% Fe	(c)	Ditto	10	Ditto
186X	About 95% Cr-6% Fe	(d)	Good adherence	35	Good adhesion except for small patch near chamber; crack near muzzle end
178X	About 90% Cr-10% Fe	(d)	Doubtful (inferior) adherence	2	Unsatisfactory adherence on one side of bore
185X	Ditto	(d)	Good adherence[f]	80[h]	Small patches of plate removed near muzzle and chamber ends
177X	"	(e)	Ditto	56[h]	Patch plus streaks of plate removed near chamber end; longitudinal cracks near muzzle
176X	"	(e)	Doubtful adherence[g]	195[h]	Small patch of nonadherent plate near the muzzle end

TABLE 3. (Continued)

Insert Number	Approximate Composition of Plate	Plating Procedure	Results of Impact and Saw-Break Tests on Segment Sawed Off Muzzle End	Number of Rounds in Firing Test	Results of Firing Tests
229X	About 90% Cr-10% Fe	(e)	Good adherence	Not completed	-
157X	Ditto	(b)	Ditto	Ditto	-
217X	90% Cr-10% Fe	(e)	"	"	-
218X	89% Cr-11% Fe	(e)	"	"	-

(a) The procedure is detailed in Appendix III, Interim Report dated October 1, 1952.
(b) The cleaning procedure is detailed in Appendix I and the plating conditions on pages 3 and 4 and Table I, Interim Report dated October 9, 1953.
(c) The cleaning procedure is detailed in Appendix I and the plating conditions on pages 10 and 11 and Table II, Interim Report dated April 9, 1954.
(d) The cleaning procedure is detailed in Appendix A and the plating conditions in Table 2, Interim Report dated October 9, 1954.
(e) The procedure is detailed in Table 1 in this report.
(f) Figure 1 is a photomicrograph illustrating good adherence after impact and saw-break testing.
(g) Figure 2 is a photomicrograph illustrating doubtful adherence after impact and saw-break testing.
(h) Firing tests on these inserts will be continued.

nickel by metallographic examination. Figure 3 is a photomicrograph of a section sawed off the breach end of the liner before dissolving out the copper. Figure 4 magnifies one of the radial cracks. There appeared to be a separation between the nickel strike deposited in the Woods-type bath for activating the chromium-iron alloy and the nickel subsequently deposited in the modified Watts-type solution. This separation between the strike and the nickel plate was the first time such a defect had occurred. It probably was due to passivation of the nickel strike surface before deposition was started in the modified Watts-type bath. Because of this defect, another insert will be electroformed for a firing test, when the research is continued, with appropriate care to prevent passivation of the nickel strike. To avoid the cracking, the hardness of the nickel plate can be reduced to about 400 Knoop.

Chromium-Alloy Plate Containing 26 to 33 Per Cent Iron

Chromium-iron-alloy plates containing 74 per cent chromium and 26 per cent iron, or 67 per cent chromium and 33 per cent iron, were obtained on cannon steel panels by making the following changes in plating conditions:

(1) Decreasing the chromium-to-iron ratio from about 40:1 to 24:1 by increasing the iron concentration to 1.45 g/l

(2) Increasing the pH from 1.95 to 2.95 (the alloy containing 33.1 per cent iron was obtained at a pH of 2.95, the other alloy at a pH of 2.72)

(3) Increasing the cathode current density from 100 to 125 amp/sq ft

(4) Providing work-bar agitation at the rate of 60 cpm using a 1-1/4-inch stroke.

These deposits were defective because they contained black streaks and blisters. The deposit containing 33.1 per cent iron had more blisters than the other. Better plate might be obtained by further modifying the plating conditions, for example, by raising the iron concentration with appropriate changes in the pH and/or bath temperature. No stress measurements were made with this alloy plate.

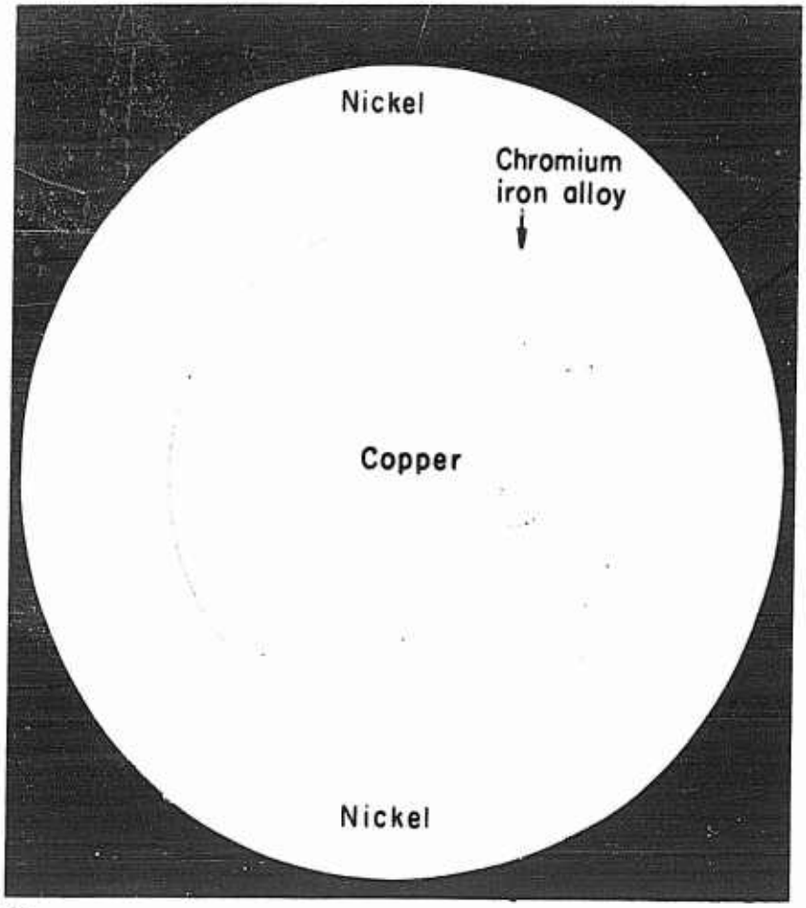

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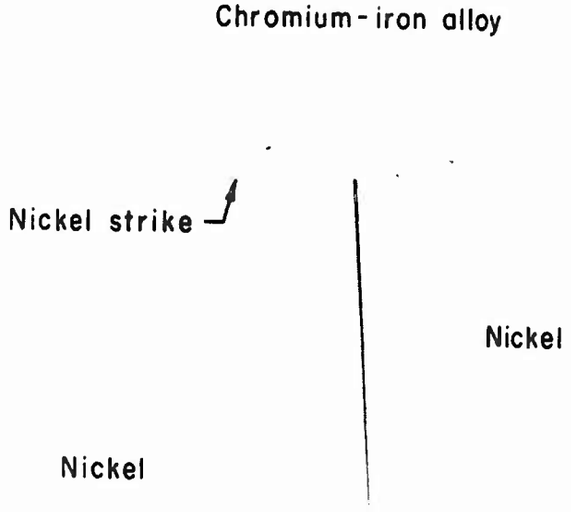
FIGURE 3. CROSS SECTION OF THE BREACH END OF AN ELECTROFORMED CHROMIUM-IRON-ALLOY EROSION-GAGE WEAPON INSERT



100X Polished – Not Etched N20174

FIGURE 4. PHOTOMICROGRAPH SHOWING CRACK IN THE NICKEL BACKUP OF THE ELECTROFORMED WEAPON INSERT SHOWN IN FIGURE 3

Hot-Hardness Measurements*

The hot hardness of chromium-iron alloy was more than that of conventional chromium at elevated temperatures. These results are shown in Figure 5. The data are detailed in Table 4.

The conventional chromium plate below 300 C was not so hard as chromium plate can be when the current density is increased. However, the hardness above 300 C would be the same regardless of the initial as-deposited value. The chromium was deposited initially at 288 amp/sq ft; however, as plating progressed and the deposit became nodular, the effective current density was lowered, thereby producing a soft deposit. The plating conditions for the chromium and chromium-iron alloys are given in the footnotes for Table 4.

WHS:DES:HLM:CLF/mm

*These data were obtained from the Sixth Technical Progress Report entitled "Electrodeposition of Chromium Alloys and Study of Elevated-Temperature Properties of Certain Electrodeposited Metals and Alloys", June 15, 1955, under Contract NOas 54-706-c, Battelle Memorial Institute, sponsored by the Bureau of Aeronautics, Navy Department.

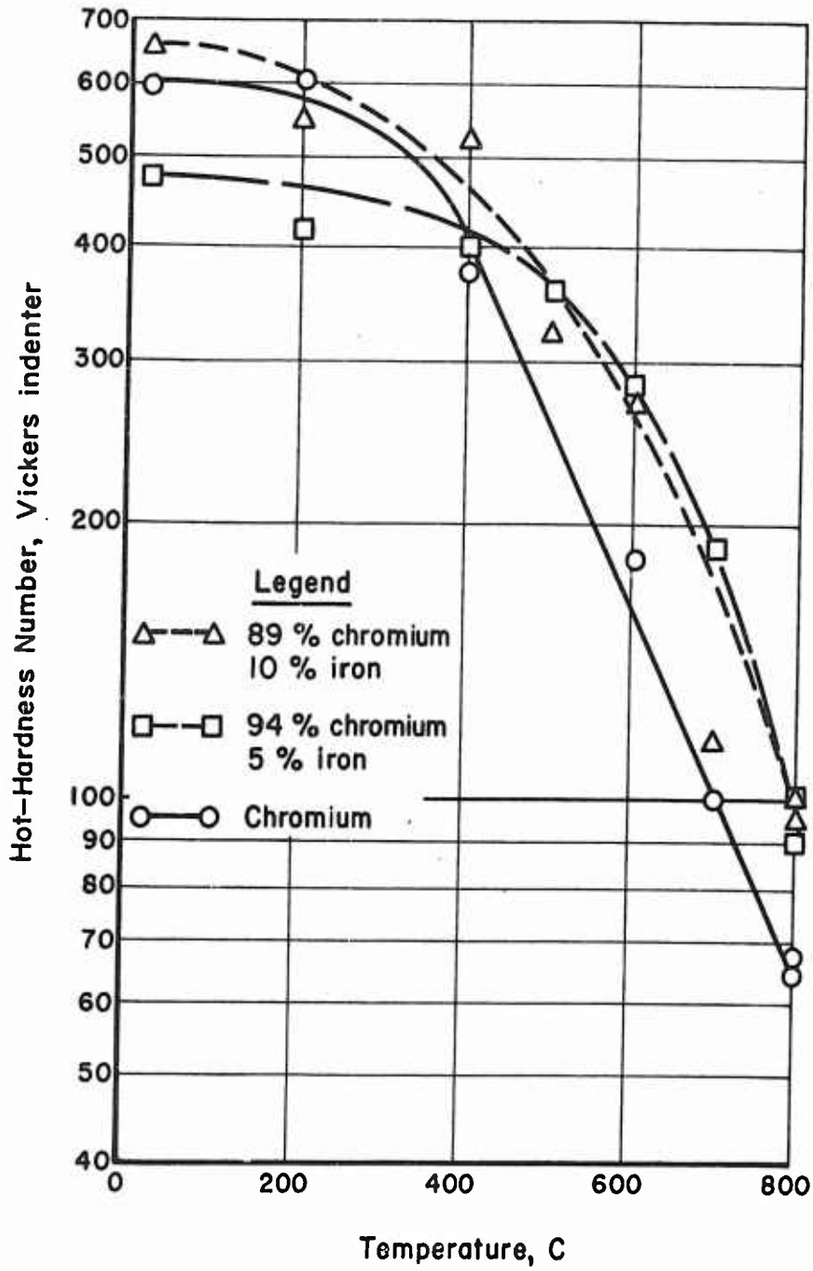


FIGURE 5. HOT HARDNESS OF CHROMIUM AND CHROMIUM-IRON ALLOY PLATE

A-15227

TABLE 4. COMPARISON OF HOT HARDNESS OF ELECTRODEPOSITED CHROMIUM-IRON ALLOY AND CHROMIUM ELECTROPLATES[a]

	Room Temperature									Elevated Temperature						
	Vickers No.			DPHN[b]		Knoop No.				DPHN[b]						
	5 kg		1 kg	0.730 kg		0.5 kg		0.1 kg		0.730 kg						
Electroplate	Before	After	Before	Before	After	Before	After	Before	After	200 C	400 C	500 C	600 C	700 C	800 C	800 C[c]
Chromium	627	261	631	594	250	616	272	662	303	608	375	291	183	100	64.4	67.5
Chromium alloy containing 10% iron	761	-	767	656	287	663	471	763	486	545	526	326	271	132	101	95.9
Chromium alloy containing 5% iron	568	-	563	474	371	533	407	531	436	420	401	360	284	187	90.9	102

(a) The chromium was deposited at 288 amp/sq ft (initially) in a bath containing 250 g/l chromic acid (CrO_3) and 2.5 g/l sulfate (SO_4) at a temperature of 130 F. The conditions for the deposition of the chromium-iron alloys were:

89% Cr, 10% Fe alloy:
350 g/l chromium ammonium sulfate [$Cr(NH_4)(SO_4)_2 \cdot 12H_2O$]
10.2 g/l ferrous ammonium sulfate [$FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$]
pH = 1.9, work-bar agitation at 32 cpm with a 1-1/4-inch stroke
Temperature = 115 F

94% Cr, 5% Fe alloy:
Same as above, except: 5.3 g/l $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$
pH = 2.0 with no agitation.

(b) Hardness impressions with ruby indenters, before and after heating to 800 C.

(c) After 15 hours at temperature. Other readings were taken shortly after each selected temperature was reached.

APPENDIX A

MODIFIED PROCEDURE FOR CLEANING AND ELECTROPOLISHING EROSION-GAGE WEAPON INSERTS

APPENDIX A

MODIFIED PROCEDURE FOR CLEANING AND ELECTROPOLISHING EROSION-GAGE WEAPON INSERTS

(1) The 1/4-inch-diameter platinum-sheathed silver anode was centered in the insert using steel end fixtures as illustrated in Figures B-1 and B-2 of the Interim Report dated October 9, 1954. These fixtures, at that time, were made of Lucite. However, because they warped during repeated use, they were replaced by steel fixtures, except for the solution input section and the Lucite anode-centering disk. Two hose clamps were used to make electrical contact to the outer surface of the tube, which was stopped off with masking tape and lacquer*. The outer surface of the fixture was stopped off with four layers of a resin coating**. Each coat was allowed to air dry for 10 to 20 minutes before being heated to 400 F for 15 minutes. The final coating was heated to 450 F for 30 minutes.

(2) The bore surface was anodically cleaned in a solution of 10 oz/gal of Anodex*** with a current density of about 100 amps/sq ft at about 180 F for 3 minutes.

(3) After rinsing with hot water, the insert was electropolished at 240 amp/sq ft in a solution containing 80 volume per cent of 85 per cent phosphoric acid and 20 volume per cent of 95 per cent sulfuric acid****. The temperature of the bath was 85 F. The specific gravity was maintained between 1.69 and 1.72. The new rifled inserts were electropolished for 30 minutes to round off the edges of the lands. The rifled inserts plated previously and stripped in hydrochloric acid solution, and the smooth-bore inserts were electropolished for 5 minutes.

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*"Gray Stonite", purchased from Stoner-Mudge, Inc., Pittsburgh 33, Pennsylvania.

**"Synthetasine 100", purchased from Bradley and Vrooman Co., 2629 S. Dearborn Street, Chicago, Illinois.

***Alkaline cleaner mixture purchased from MacDermid, Inc., Waterbury, Connecticut.

****This electropolishing process is disclosed in U.S. Patent 2,334,699, owned by Battelle Development Corporation. It is to be understood that disclosure in this report does not constitute nor imply the grant of a license to use this process.

(4) After rinsing in cold water, the insert was again anodically cleaned in the Anodex solution for 3 minutes.

(5) After rinsing in hot water, the insert was dipped for 1 minute in a 10 per cent solution of hydrochloric acid.

(6) The next step was either the "Quick-Water Rinse" or the "Dilute Acid Dip":

(a) The Quick-Water Rinse consisted of rinsing the insert with cold tap water for about 15 seconds before placing it in the plating bath.

(b) The Dilute Acid Dip consisted of immersing the insert in a solution containing 18 ml/l of 95 per cent sulfuric acid for 1 minute. The insert was then placed in the plating bath with no subsequent rinsing.

(7) Filtered plating solution was pumped through the insert for about 1 minute in each case before deposition was started.

APPENDIX B

PROCESSES INVESTIGATED TO IMPROVE ADHERENCE OF CHROMIUM-IRON ALLOY TO CANNON STEEL

APPENDIX B

PROCESSES INVESTIGATED TO IMPROVE ADHERENCE OF CHROMIUM-IRON ALLOY TO CANNON STEEL

Introduction

The procedures described herein for preparing steel for plating were evaluated on 2 x 6-inch cannon steel (SAE 4135 designation) flat panels. The adherence was judged by saw-break tests on sections of the steel that were plated with 0.003 to 0.005 inch of the chromium-iron alloy.

A plastic shield was used to keep the current density uniform on each panel. This shield was described in the Interim Report dated April 9, 1954. The plating process corresponded to the procedure detailed in Appendix C.

Effects of Changing the Preparation Procedure

Activating Acid Dip

Good adherence of chromium-iron alloy to cannon steel panels was obtained after heat treating the plated steel if the steel panels were rinsed in a dilute sulfuric acid solution with no subsequent rinse just before plating. The dilute acid solution contained 18 ml/l of sulfuric acid (sp gr = 1.84) in distilled water; the pH of the solution was 0.8.

Table B-1 details the results of the adherence tests on nine panels plated after dipping in the dilute sulfuric acid solution. For comparison, Table B-2 shows the results of adherence tests on plates produced without the activating dip. The dilute acid evidently inhibited the formation of the hydrated ferrous oxide film which causes poor adherence, but did not completely eliminate the film, because heat treatment was required to secure good adherence.

TABLE B-1. ADHERENCE OF CHROMIUM-IRON-ALLOY DEPOSITS ON STEEL PANELS USING THE DILUTE ACID DIP PREPLATING PROCEDURE[a]

Sample Number	Adherence Tests: Before Heat Treatment, Chisel Test	Adherence Tests: Before Heat Treatment, Saw-Break Test[c]	Adherence Tests: After Heat Treatment[b], Chisel Test	Adherence Tests: After Heat Treatment[b], Saw-Break Test[c]	Condition of Chromium-Iron-Alloy Deposit
9509-					
90B	Doubtful adherence	Nonadherent	Adherent	Adherent	A few small flaky spots near top on both sides, small cracked area in center of both sides, both ph = 1.65
91A	Ditto	"	Doubtful adherence	Ditto	Good appearance, a few small cracks on bottom edge near corner and near top on one side
91C	Nonadherent	"	Adherent	"	Good appearance, no cracking or blistering
10160-					
16C	Doubtful adherence	"	"	"	Ditto
16E	Nonadherent	"	"	"	"
17B	"	"	"	"	"
18B	"	"	"	"	"
18E	"	"	"	Doubtful adherence	"
19A	"	"	"	Adherent	"
Per cent nonadherent	66.7	100	0	0	
Per cent doubtful	33.3	0	11.1	11.1	
Per cent adherent	0	0	89.9	88.9	

Footnotes appear on the following page.

Footnotes for Table B-1

(a) Standard preplating procedures were the same as given in Appendix A except the dilute acid dip was used in each case. Constant plating conditions were:

300 to 350 g/l chromium ammonium sulfate [$Cr(NH_4)(SO_4)_2 \cdot 12H_2O$]
100 g/l ammonium sulfate [$(NH_4)_2SO_4$]
5.3 to 6.2 g/l ferrous ammonium sulfate [$Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$]
ph = 1.85 to 2.0
Temperature = 115 F
Cathode current density = 100 amp/sq ft
A 1-inch shield of Lucite was used at the cathode
No agitation
Plating bath was dummied at 100 amp/sq ft for 1 hour each day before plating any panels
Anodes (2) were platinum sheet (1" x 4") in porous cups
Redox poise = neg. Fe^{3+}; neg. Cr^{6+}
Volume of bath = 15.1.

(b) The heat treatment procedure was to heat in a hydrogen atmosphere for 1 hour at 350 F and then for 3 hours at 750 F.

(c) The saw-break test consisted of sawing the panel part way through and then breaking it the rest of the way, producing two segments. The fracture zone was examined metallographically.

TABLE B-2. ADHERENCE OF CHROMIUM-IRON-ALLOY DEPOSITS ON STEEL PANELS CLEANED AND ELECTROPOLISHED BUT NOT ACTIVATED BEFORE PLATING(a)

Sample Number	Adherence Tests: Before Heat Treatment, Chisel Test	Before Heat Treatment, Saw-Break Test(c)	After Heat Treatment(b), Chisel Test	After Heat Treatment(b), Saw-Break Test(c)	Condition of Chromium-Iron-Alloy Deposit
9509-					
71C	Nonadherent	Nonadherent	Nonadherent	Nonadherent	Good appearance, no cracking or blistering
97B	"	"	Adherent	Adherent	Ditto
98C	"	"	"	"	Five small blisters on one side, a few black streaks
98E	"	"	"	"	A few small, scattered blisters on both sides
10160-					
9E	"	"	"	Doubtful adherence	Dark with many small, scattered nodules; no cracks or blisters
10C	"	"	Nonadherent	Adherent	Lustrous; many small, hairline cracks along edges of both sides
10E	"	"	Adherent	Doubtful adherence	Good appearance; a few small cracks on one edge of one side
13B	"	"	Adherent	Adherent	Dark, no cracks or blisters
18G	"	"	Nonadherent	Adherent	Blistering and flaking on bottom corners
Per cent nonadherent	100	100	33.3	11.1	
Per cent doubtful	0	0	0	22.2	
Per cent adherent	0	0	66.7	66.7	

Footnotes appear on the following page.

Footnotes for Table B-2

(a) Standard preplating procedures were the same as given in Appendix A except the dilute acid dip was used in each core. Constant plating conditions were:

300 to 350 g/l chromium ammonium sulfate [$Cr(NH_4)(SO_4)_2 \cdot 12H_2O$]
100 g/l ammonium sulfate [$(NH_4)_2SO_4$]
5.3 to 6.2 g/l ferrous ammonium sulfate [$Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$]
pH = 1.85 to 2.0
Temperature = 115 F
Cathode current density = 100 amp/sq ft
A 1-inch shield of Lucite was used at the cathode
No agitation
Plating bath was dummied at 100 amp/sq ft for 1 hour each day before plating any panels
Anodes (2) were platinum sheet (1" x 4") in porous cups
Redox poise = neg. Fe^{3+}; neg. Cr^{6+}
Volume of Bath = 15 l.

(b) The heat treatment procedure was to heat in a hydrogen atmosphere for 1 hour at 350 F and then for 3 hours at 750 F.

(c) The saw-break test consisted of sawing the panel part way through and then breaking it the rest of the way, producing two segments. The fracture zone was examined metallographically.

Entering Plating Bath With Current On

Another modification of the usual preplating procedures was investigated in conjunction with the dilute acid dip. By completing the electrical connection to the cathode and anodes before immersing the cathode in the plating bath, good adherence of nine plates was obtained on nine panels. These steel panels were also dipped in the dilute acid solution as a final rinse just before plating. An auxiliary cathode was used seven times to keep the current density constant at 100 amp/sq ft. As each panel was lowered into the plating bath, the auxiliary panel, which was already in the bath with the current on, was withdrawn at the same speed. Two panels were plated without the auxiliary cathode; the plate on these was slightly blistered at the corners.

Phosphoric Acid Anodic Treatment

Good adherence without heat treatment was obtained on one panel prepared for plating by preceding the dilute sulfuric acid dip with an anodic treatment at 100 amp/sq ft for five minutes in a 42.5 per cent solution of phosphoric acid and distilled water (50 per cent by volume of 85 per cent acid) at a temperature of 110 F*. The panel was then rinsed, dipped in 10 per cent hydrochloric acid for 1 minute, rinsed, and finally dipped in the dilute sulfuric acid solution (18 ml/l sulfuric acid) for 1 minute before plating. Metallographic examination after the saw-break test showed no evidence of poor adhesion of the plate without the heat treatment. Another panel which had been treated in the same manner, except for omitting the hydrochloric acid and dilute acid dips, showed poor adhesion without the heat treatment.

After the anodic treatment with phosphoric acid, the panel was inactive in the acid dips and, thus, probably was inactive in the plating bath. This passive condition probably is due to a very thin phosphate coating. It evidently prevented the formation of any hydrated ferrous oxide and thereby promoted good adherence between the steel and the chromium-iron-alloy deposit.

* This process is used to obtain adherence deposits of silver directly on steel; it is disclosed by William M. Martz, U. S. Patent 2,431,947, issued December 2, 1947, General Motors Corporation.

Sulfuric Acid Anodic Treatment

Adhesion of chromium-iron-alloy plate on steel was unsatisfactory without heat treatment when sulfuric acid was substituted for phosphoric acid in the anodic treatment at 100 amp/sq ft. Poor adhesion was revealed by saw-break testing two panels that were treated anodically for 5 minutes in a 20 per cent (by volume) solution of sulfuric acid at a temperature of 74 F prior to plating with chromium-iron alloy. The steel panels were active in the subsequent hydrochloric acid dip.

Nickel-Strike Plate

Plating SAE 4135 steel panels with a 0.00015-inch nickel strike, prior to plating with chromium-iron alloy, caused inferior adherence after heat treatment. Among nine panels plated with nickel, the chromium-iron plate on only one was free of defects; two chromium-alloy plates were completely blistered and peeled; the rest were cracked, blistered, and flaky. Among the seven panels that were heat treated, only three deposits adhered satisfactorily, judging by the saw-break tests. Chromium-iron alloy plates on two panels described in the Interim Report dated October 9, 1954, were unsatisfactory in adherence. The nickel-plating procedures were detailed in that report.

Vapor Blasting

Substituting vapor blasting for electropolishing did not improve the adherence of the chromium-iron deposit before or after heat treatment. Two SAE 4135 steel panels were cleaned, vapor blasted, recleaned, acid dipped, dilute acid dipped, and then plated. Metallographic examination after heat treatment showed that only one plate had satisfactory adherence. In work reported previously (Interim Report dated October 9, 1954), the panels were not recleaned after vapor blasting. The adherence of those deposits was also unsatisfactory.

Sulfurous Acid Dip

Rinsing SAE 4135 steel panels in a solution saturated with sulfur dioxide and also containing 18 ml/l of sulfuric acid caused very poor adherence of the subsequent chromium-iron-alloy deposit. Colloidal sulfur was formed in the SO_2 dip; because no rinse was used thereafter, sulfur particles were carried into the plating bath, causing the poor deposits.

Hydroxylamine Hydrochloride Dip

A dip in a solution containing 50 g/l of 200 g/l hydroxylamine hydrochloride, and 18 ml/l of sulfuric acid caused peeling and blistering.

Other Changes

Three other surface preparation processes were reported in the Interim Report of October 9, 1954. The processes were the addition of sodium silicate to the rinse water, alkaline derusting, and an iron-strike plate. None of these treatments produced an adherent deposit, even after the usual heat treatment.

Results of Adding Iron Complexing Agents to the Plating Bath

Agents for complexing iron were investigated as additives to the chromium-iron plating bath for promoting adherence of the plate. Triethanolamine, potassium ferrocyanide, and boric acid were the agents investigated. None of the chromium-iron plates produced with these addition agents in the plating bath were adherent. Triethanolamine (15 g/l) reduced the cathode efficiency and the plating range, causing flaky and nonadherent deposits. Boric acid (5 or 30 g/l) had no effect on the adherence or appearance of the deposits, but potassium ferrocyanide (5 g/l) in the plating bath caused a large reduction in the plating range and in the cathode efficiency.

APPENDIX C

SUMMARY OF RECOMMENDED PROCEDURES FOR OBTAINING SOUND CHROMIUM-IRON-ALLOY DEPOSITS ON EROSION-GAGE WEAPON INSERTS

APPENDIX C

SUMMARY OF RECOMMENDED PROCEDURES FOR OBTAINING SOUND CHROMIUM-IRON-ALLOY DEPOSITS ON EROSION-GAGE WEAPON INSERTS

Procedure for Preparing the Chromium-Iron-Alloy Plating Baths

The procedure recommended for preparing a 36-liter bath: chromium-iron-alloy plating baths was as follows:

(1) About 20 liters of distilled water were heated to boiling.

(2) Twenty-eight pounds of chromium ammonium sulfate [350 g/l $Cr(NH_4)(SO_4)_2 \cdot 12H_2O$]* were added to the hot water with vigorous stirring by a mechanical stirrer.

(3) Eight and one-third pounds of ammonium sulfate [100 g/l $(NH_4)_2SO_4$] were added with vigorous stirring.

(4) After cooling the solution to about 100 F or less, a 5-liter solution containing 1800 grams of sulfamic acid neutralized with ammonium hydroxide (to a pH of 2.0) was added to the chromium-iron plating bath.

(5) One-half pound of ferrous ammonium sulfate [6.3 g/l $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$] was added with stirring. (If Technical Grade chromium ammonium sulfate is used, analyze for iron before making this addition.)

(6) The pH of the solution was raised to 2.0 by adding 29 per cent ammonia solution in water. Approximately 500 ml of the ammonia solution were required, equivalent to 13.4 ml of 29 per cent ammonia solution per liter of bath. (The pH is measured with a 30-ml sample quickly cooled to about 90 F. The reading is taken 15 to 20 seconds after immersion of the glass and calomel electrodes. To avoid poisoning the glass electrode, it should not be immersed in the solution longer than 5 minutes.)

*Purchased from the Mutual Chemical Company, Baltimore, Maryland.

(7) Approximately 150 grams of activated carbon* were wetted with about 500 ml of distilled water and stirred into the plating solution. Stirring was continued for about 1 hour at about 160 F.

(8) Using Polycel** for a filter agent, the solution was filtered into the Pyrex jar used for the plating tank. Distilled water was added to adjust the volume of the bath to 36 liters.

(9) After adjusting the temperature to 115 ± 3 F, the bath was electrolytically purified for 48 hours, using a steel cathode with about 1 square foot of area and a current of 5 amperes. An alternative purification procedure used successfully for a 15-liter bath consisted of electrolyzing with a current density of 100 amp/sq ft (1 ampere per liter of bath) for 3 hours. Copper reduced at the cathode in sponge form deposited on the wall of the tank and the plastic shield surrounding the cathode, or floated on top of the bath. It was removed by filtering the bath.

After following the above procedure, the pH should be raised by adding 10 per cent ammonia solution, to reach the following values:

For plating smooth bore inserts or flat panels	2.0 to 2.1
For plating rifled inserts	2.1 to 2.4
For plating smooth bore, 40-mm sections	2.2

About 10 ml of 10 per cent ammonia solution/liter increases the pH by 0.1 unit after thorough stirring to dissolve chromic hydroxide. (One ml of 95 per cent sulfuric acid/liter lowers the pH about 0.1 unit.)

When preparing a new bath or after making chemical additions to an aged bath, it should be dummied at 100 amp/sq ft (1 ampere per liter of bath) for 2 to 4 hours to remove impurities.

*Darco 51, purchased from the Darco Department of the Atlas Powder Company, New York, New York.
**Purchased from the West Virginia Pulp and Paper Company, Industrial Chemical Sales Division, New York, New York.

Maintenance and Operating Conditions

The bath constituents should be maintained within the following limits:

Constituent	Minimum	Maximum
Chromium (Cr^{3+}), g/l	35	40
Iron (Fe^{2+})*, g/l	0.80	0.90
Ammonium ion (NH_4^+), g/l	50	80

The following operating conditions are recommended for plating erosion-gage weapon.

Cathode current density	100 to 115 amp/sq ft
Temperature**	113 to 117 F
Flow rate***	0.25 to 0.30 gal/min

Analytical Procedures

Chromium

A colorimetric method is recommended for determining the concentration of chromium as follows:

(1) A 1-ml sample of the plating bath is diluted to 100 ml with distilled water in a volumetric flask and a 1-ml aliquot is oxidized with 4 ml of 60 per cent perchloric acid.

(2) The oxidized solution is diluted to exactly 10 ml; its optical density is measured at 420 mμ.

*The iron should always be maintained in the reduced state (Fe^{2+}). Should iron become oxidized to Fe^{3+} by air oxidation or by faulty operating technique, it must be reduced to Fe^{2+} by plating a flat panel between anodes suspended in porous alundum cups, such as RA 84, No. 10040 Cups, made by the Norton Company, Worcester, Massachusetts. The cups are filled with a solution containing 100 g/l of ammonium sulfate plus 2 g/l of 95 per cent sulfuric acid. Plastic shields, such as described in the Interim Report dated April 9, 1954, should be used to keep the current density uniform on the flat panels.

**This temperature should be maintained at all times to prevent a shift in the equilibrium between the green and violet chromium complex compounds. Otherwise, defective plates will occur. Should the bath become excessively cooled, accidentally, it must be heated to boiling, filtered through activated carbon, and electrolyzed 2 to 4 hours (1 ampere/liter) to restore the equilibrium between the complex chromium compounds.

***Based on a 12-inch insert; air should be excluded to avoid a defective plate.

(3) The optical density is converted to concentration by comparison with a chart prepared by measuring the optical densities of standard solutions of potassium dichromate treated with perchloric acid. (A standard solution containing 0.0517 g/l of chromium gave an optical-density reading of 2.46; a standard solution containing 0.1034 g/l of chromium gave a reading of 4.92.)

Iron

The concentration of ferrous iron is determined as follows:

Reagents

10 per cent sulfuric acid, by volume
1 per cent solution of hydroquinone in water (freshly prepared), or a small amount of the crystals
0.1 per cent solution of o-phenanthroline monohydrate in water
25 per cent sodium citrate solution.

Procedure

(1) A 1-ml sample of the plating bath is diluted to 100 ml in a volumetric flask.

(2) To a 1-ml aliquot of the diluted plating solution, 4 drops of the dilute sulfuric acid, 15 drops of the hydroquinone solution, or a small amount of the crystals, 20 drops of the o-phenanthroline solution, and 12 drops of the sodium citrate solution are added.

(3) The combined solution is diluted to 10 ml.

(4) After 10 minutes, the optical density is determined at 490 mμ with a 490-mμ filter.

(5) The optical density is converted to concentration by comparison with a chart prepared by measuring the optical densities of standard ferrous ammonium sulfate solutions at 490 mμ. (A standard solution of 25 mg/l of iron gave a reading of 5.6; a standard containing 12.5 mg/l of iron gave a reading of 2.98. A blank solution gave a reading of 0.25.)

Copper

Reagents

Dithizone (diphenylthiocarbazone): 50 mg/l in carbon tetrachloride

Hydroxylamine hydrochloride: 200 g/l in water (freshly prepared)

Procedure. One ml of dithizone reagent and 1 ml of the hydroxylamine hydrochloride solution were placed in each of two test tubes. One drop of the plating bath was added to one of the test tubes. Both tubes were shaken vigorously for about 1 minute. A change in the color of the dithizone "blank" would indicate contamination of one or the other reagent, or of the test tubes. One mg/l of copper gave a pale-violet color; 30 mg/l or more of copper caused the appearance of a strong violet color.

Sensitivity. About 1 mg or more of copper per liter of bath was detected by this method. Freshly prepared chromium-iron baths gave a positive test for copper because of the copper content of the chromium ammonium sulfate, which was 0.005 per cent by weight or less. Dummying the baths for 2 to 4 hours reduced the copper concentration below the concentration detected by the dithizone test. A copper concentration of about 15 mg/l had no apparent harmful effect on the chromium-iron plate. More than about 30 mg/l of copper caused inferior plate.

Removal of Copper. The copper can be removed by either of two methods as follows: (1) one method is to dummy the bath overnight at 5 amp/sq ft or until no more black copper oxide is deposited on a clean panel; (2) the other method is to dummy the bath at 100 amp/sq ft (1 amp/liter of bath) for two to four hours. This treatment will reduce the copper to metallic powder which must then be filtered out of the bath. The copper powder must also be wiped from the sides of the tank and the heat exchangers.

Effects of Other Impurities

Nickel, lead, and other metallic impurities* are also detrimental to the chromium-iron plating bath. Purification may be effected by precipitation with hydrogen sulfide followed by an activated-carbon treatment to remove the excess.

*A complete list is given in the Interim Report dated April 9, 1954, page 42.

Effects of Organic Impurities

Oil, grease, and other organic impurities cause a decrease in cathode efficiency, a loss in throwing power, and/or pitting. They can be removed by activated carbon which is added to the cake in the filtering unit. However, frequent changes of this filter cake are needed to be effective. When characteristically poor deposits are obtained (that cannot be attributed to other impurities), the bath should be treated with 5 g/l of activated carbon* at about 180 F, stirring for 1 to 2 hours before filtering.

*Darco, grade S-51.

APPENDIX D

PROCEDURE FOR PLATING EROSION-GAGE WEAPON INSERTS WITH CONVENTIONAL CHROMIUM

APPENDIX D

PROCEDURE FOR PLATING EROSION-GAGE WEAPON INSERTS WITH CONVENTIONAL CHROMIUM

Plating Bath and Conditions

400 g/l chromic acid (CrO_3)

4 g/l sulfuric acid (H_2SO_4)

Specific gravity = 1.28 at 72 F

Temperature of bath = 130 F

Cathode current density = 300 amp/sq ft

Plating rate = 0.007 inch/hour

Volume of bath = 35 liters

Anode was a 94-6 lead-tin coated steel rod, threaded at both ends so a tensile stress could be applied to keep it straight.

Preplating Procedures

(1) The bath was dummied at 300 amp/sq ft for 2 hours after initial make-up.

(2) The inserts were cleaned anodically at 100 amp/sq ft for 3 minutes in a solution of 10 oz/gal of Anodix at a temperature of about 180 F.

(3) After rinsing in warm water, Insert 224X was electropolished for 5 minutes and Insert 216X was electropolished for 1 hour at 225 amp/sq ft in the solution described in Appendix A, Step 3.

(4) After a cool-water rinse, the lead-alloy plated steel electrode used in Step 3 was removed from the fixture and another lead-alloy plated steel anode was inserted in its place.

(5) Same as Step 2.

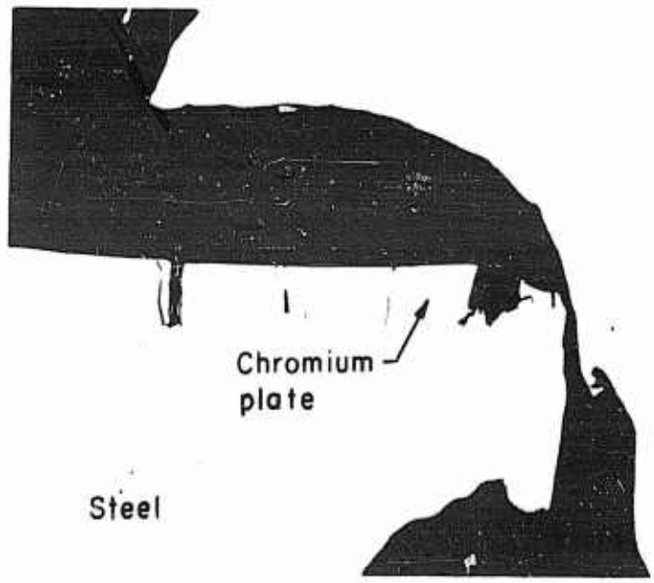
(6) After rinsing in warm water, the inserts were dipped for a few seconds in a 10 per cent solution of hydrochloric acid.

(7) After a quick (about 15 seconds) cool-water rinse, the insert was placed in the chromium-plating bath. The inserts were treated anodically for about 30 seconds at 150 amp/sq ft before being plated (cathodically) at 300 amp/sq ft.

Physical Properties of the Chromium Deposits

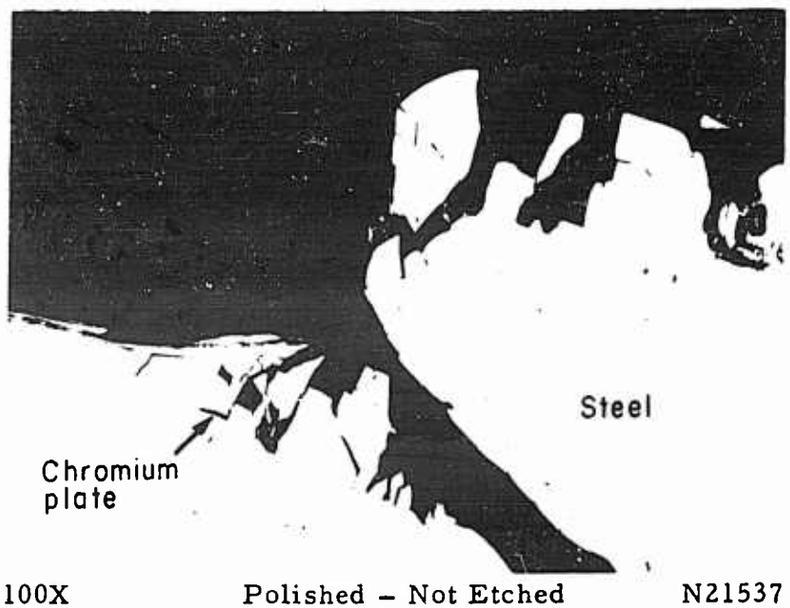
The plate on each insert was adherent, according to the chisel and saw-break tests. However, the deposits cracked and fractured near the saw-break edges as shown in Figures D-1 and D-2. The thickness and hardness of the chromium deposits were:

Insert No.	Thickness, inch	Knoop Hardness (100-Gram Load)
224 X	0.0022 to 0.0030	850 to 899
216 X	0.0060 to 0.0070 (Lands) 0.0050 to 0.0060 (Grooves)	863 to 917



100X Polished – Not Etched N21536

FIGURE D-1. CHROMIUM DEPOSIT ON SMOOTH-BORE EROSION-GAGE WEAPON INSERT NO. 224X AFTER SAW-BREAK TESTING



100X Polished – Not Etched N21537

FIGURE D-2. CHROMIUM DEPOSIT ON RIFLED EROSION-GAGE WEAPON INSERT NO. 216X AFTER SAW-BREAK TESTING

APPENDIX E

PROCEDURE FOR ELECTROFORMING EROSION-GAGE WEAPON INSERTS

APPENDIX E

PROCEDURE FOR ELECTROFORMING EROSION-GAGE WEAPON INSERTS

A smooth-bore erosion-gage weapon insert was produced by plating chromium-iron alloy on a copper mandrel, backing up the alloy deposit with a hard electrodeposited nickel alloy*, and then dissolving the copper mandrel. The electroformed liner consisted of a layer of chromium-iron alloy, 0.020 to 0.024-inch thick, backed up with 5/32 to 7/32-inch of nickel alloy with a hardness of 422 to 487 Knoop (100-gram load). After electrodepositing the nickel, the insert was turned down to a diameter of 1.105 inches and the copper mandrel partially removed by drilling with a 3/16-inch drill. The rest of the copper was dissolved in nitric acid solution (1:1 at 50 to 80 F).

The adherence of the chromium-iron alloy was unsatisfactory near the muzzle end, due to the changes in the solution level during plating which exposed the end of the insert and caused a series of laminations in the chromium-iron alloy. The nickel-alloy backup was separated from the nickel strike for about one-half the circumference. This condition existed at both ends of the insert. The rupture might have occurred within the nickel strike which has a low yield strength. A thinner strike plate will be used in future electroforming operations.

The 36-liter chromium-iron plating bath contained: 330 g/l chromium ammonium sulfate, 6.0 g/l ferrous ammonium sulfate, and 100 g/l ammonium sulfate. The pH was 2.0; the bath was dummied for 3 hours at 100 amp/sq ft (45 ampere-hours) at a temperature of 114 F before plating a dummy mandrel for 1 hour. The dummy mandrel was satisfactory; thereafter, the polished mandrel was cleaned in Anodex (8 oz/gal at 180 F) at 50 amp/sq ft for 2 minutes, rinsed with warm water, dipped in a 10 per cent solution of hydrochloric acid for about 30 seconds, rinsed in cool water, then placed in the plating bath with the current on at 5 amp/sq ft (to prevent dissolution of copper) and, after centering between the four anodes (lead strips in porous cups), the current was raised to 100 amp/ sq ft. After depositing the chromium-iron alloy in 20 hours, the mandrel was rinsed and plated for 25 minutes at 100 amp/sq ft in a nickel strike bath consisting of 240 g/l nickel chloride and 50 ml/l of 36 per cent by weight hydrochloric acid solution. Temperature of the bath was 80 F. The mandrel was then rinsed and placed in the nickel-alloy plating bath containing:

*The alloy is about 10 per cent iron, 1 per cent zinc, balance nickel. Rights to use the process under patents applied for have been acquired by The Battelle Development Corporation. It is to be understood that disclosure in this report does not constitute nor imply the grant of a license to use this process.

300 g/l $NiSO_4 \cdot 6H_2O$

30 g/l $NiCl_2 \cdot 6H_2O$

42 g/l H_3BO_3

11 g/l Standard Nickel Brightener A

3.5 g/l Standard Nickel Brightener B

3.0 g/l Standard Nickel Brightener C

1.0 per cent by volume XXXD wetting agent*.

The insert was removed every 24 hours to remove and smoothen out defects by mechanical polishing. After polishing and cleaning, the surface of the nickel was activated by electropolishing prior to plating more nickel.

Further attempts at electroforming an insert were not successful due to the excessive porosity of the anode cups, which allowed hexavalent chromium to diffuse from the anolyte into the plating bath and thereby produced unfavorable conditions for obtaining a sound chromium-iron deposit. Anode cups with a greater density will be used in future electroforming investigations.

*Purchased from the Horsbow Chemical Company, Cleveland, Ohio